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THE EAGLE-PICHER COMPANY • COUPLES DEPARTMENT: JOPLIN, MISSOURI

INVESTIGATIONS LEADING TO THE
DESIGN AND DEVELOPMENT OF
MAGNESIUM/MAGNESIUM PERCHLORATE BATTERIES
JANUARY 1, 1965 THROUGH MARCH 31, 1965
REPORT NO. 3
THIRD QUARTERLY PROGRESS REPORT
CONTRACT NO. DA-28-043-AMC-00271(E)

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DESIGN AND DEVELOPMENT OF
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JANUARY 1, 1965 THROUGH MARCH 31, 1965

CONTRACT NO. DA-28-043-AMC-00221(E)

DEPARTMENT OF THE ARMY PROJECT NO. 1G622001 A0530200

USAEL TECHNICAL GUIDELINES
EPP NO. 58274
DATED JUNE 20, 1964

U. S. ARMY ELECTRONICS COMMAND
POWER SOURCES DIVISION, ELECTRONICS COMPONENTS LABORATORY
FORT MONMOUTH, NEW JERSEY

THE EAGLE-PICHER COMPANY
COUPLES DEPARTMENT
P. O. BOX 47
JOPLIN, MISSOURI

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J. M. Dines, Engineering Manager

DATE OF REPORT: April 30, 1965

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I. PURPOSE

The purpose of this work is to conduct investigations which will lead to the development of reliable, production feasible magnesium/magnesium-perchlorate batteries; to carry on research and development on the use of magnesium perchlorate as an electrolyte, and to determine the applicability of the system in military field use.

The investigations should provide practical design information which can be used for future battery development.

II. ABSTRACT

This abstract describes the significant accomplishments made on the research and development of magnesium/magnesium perchlorate batteries during the past three months.

Research on the development of the AN/PRC-62, AN/PRC-25, and PPS-5 have been carried out and considerable advancement has been made. Batteries for each application have been constructed and discharged.

The program was directed toward attaining the optimum performance over a temperature range of -40° F to +125° F. Research in relation to additives was continued.

Eagle-Picher battery numbers have been assigned to each application:

AN/PRC-62 .... MAP-2014
AN/PRC-25 .... MAP-2018
PPS-5 .... MAP-2019

III. REFERENCES AND CONFERENCES

A conference was held at the U. S. Army Electronics Command, Electronic Components Laboratory, Fort Monmouth, on February 3, 1965. Mr. N. T. Wilburn, Dr. A. Fischbach, and Mr. R. McCutcheon represented USAEL and Mr. E. B. Cupp represented The Eagle-Picher Company. Progress on the design and development of the three field applications were discussed.

IV. INTRODUCTION

The major effort during the past quarter has been directed toward establishing definite battery designs to meet the three field applications.

The major effort was directed toward MAP-2018 (25) and modular construction of MAP-2014 (62). Battery designs were developed that would meet the desired specifications.

Effort was then directed towards refining the design of MAP-2019 (5). Discharge temperature, anode corrosion, and electrolyte evaporation are still the critical points under study.

V. FACTUAL DATA AND DISCUSSION

A. Development of MAP-2018 (25)

A large portion of the quarter was spent developing a battery that would meet the specifications of MAP-2018 (25). The overall cell design is comparatively the same as the cells used in MAP-2014 (62). The differences are in the additives and anode type.

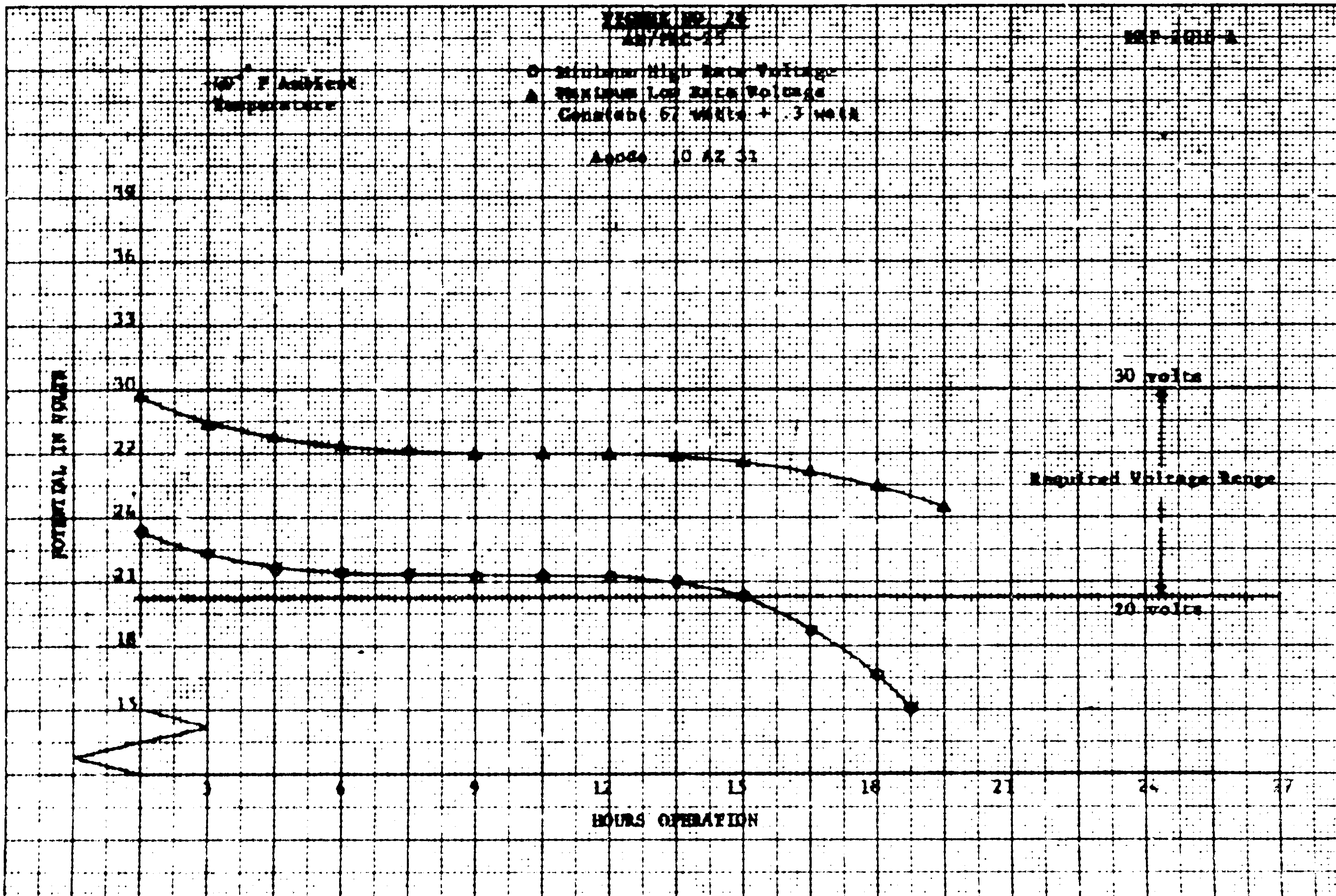
During the initial stages of this battery design the same identical cells that are used in MAP-2014 (62) were utilized in MAP-2018 (25) and discharged at the specific rates (Figure No. 26).

Figure No. 26 is a curve of discharge characteristics of the above battery construction when discharged at -40° F. During the discharge the battery lost more heat during the low rate discharge than it gained during the high rate discharge. Therefore, the battery voltage fell below the required minimum.

Since commercial pure magnesium has a higher corrosion rate which produces higher temperatures during discharge, it was decided to use pure magnesium instead of AZ 31 to increase the heat dissipation. A battery was constructed utilizing pure magnesium and discharged at -40° F. This unit became too hot and did not meet specifications (Figure No. 27).

Due to the heat gained with C. P. magnesium and heat loss with AZ 31 it was decided to construct a unit utilizing one-half AZ 31 and one-half C. P. magnesium to obtain an equilibrium between the two types of anodes. The heat lost was not enough to equalize the heat gained, and therefore this unit also became too hot (Figure No. 28).

Another approach was to use Li_2CrO_4 as an additive to inhibit the rapid corrosion rate of C. P. magnesium. A unit was constructed utilizing the .015" C. P. magnesium and 1% Li_2CrO_4 by weight. After eighteen and one-half hours of discharge this unit fell below minimum voltage. Inspection of the


Maximum Low Rate Voltage
Anode 10 AZ 31
POTENTIAL IN VOLTS
39
36
33
30
27
24
21
18
15
3
6
9
12
15
18
21
24
27
HOURS OPERATION
30 volts
Required Voltage Range
20 volts

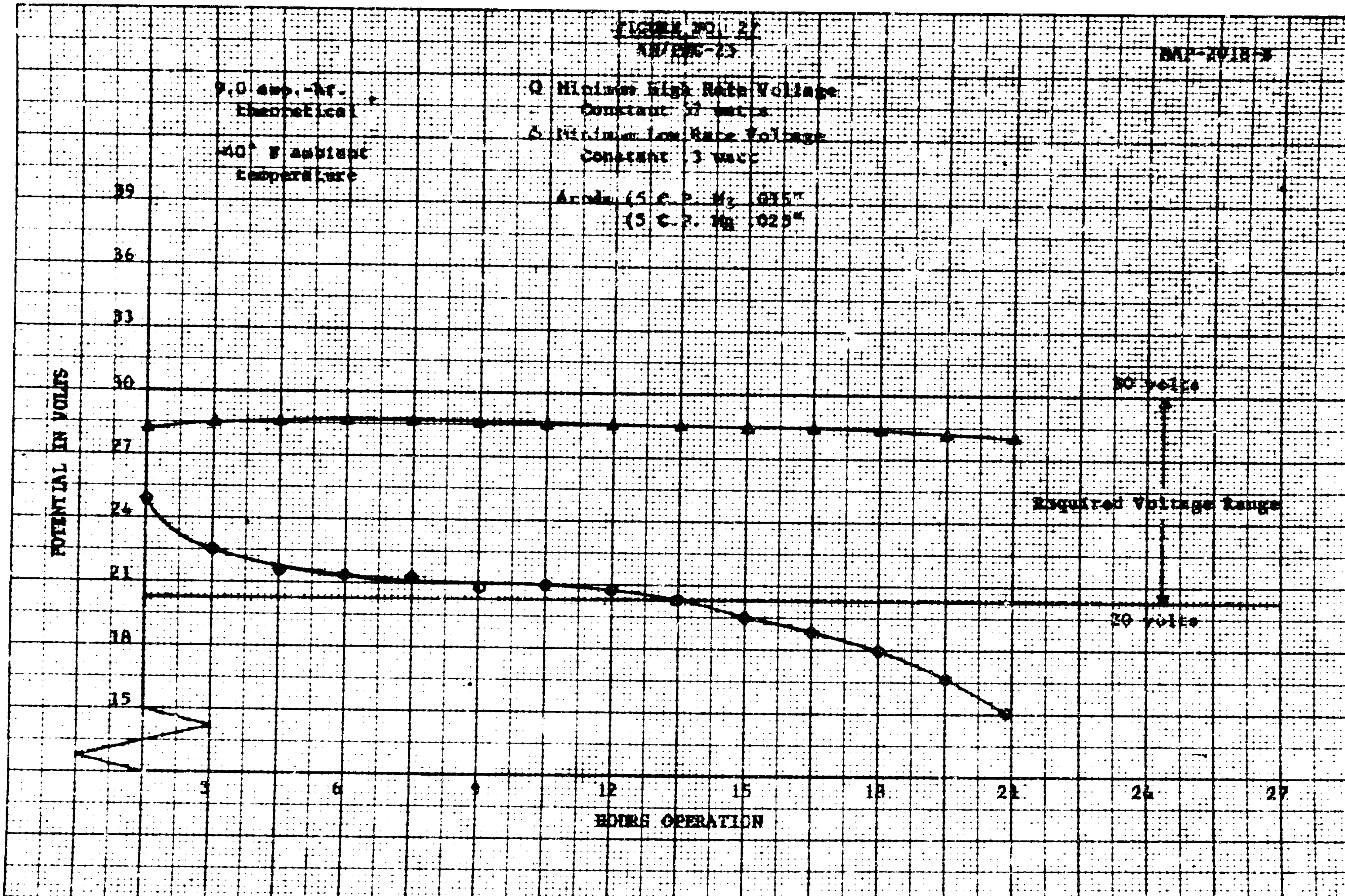


FIGURE NO. 27
Minimum High Rate Voltage
Constant
Minimum Low Rate Voltage
Constant 3
9.0 amp.-hr.
theoretical
-40° F ambient
temperature
Required Voltage Range
30 volts
20 volts
POTENTIAL IN VOLTS
15
18
21
24
27
30
33
36
39
3
6
9
12
15
18
21
24
27
HOURS OPERATION

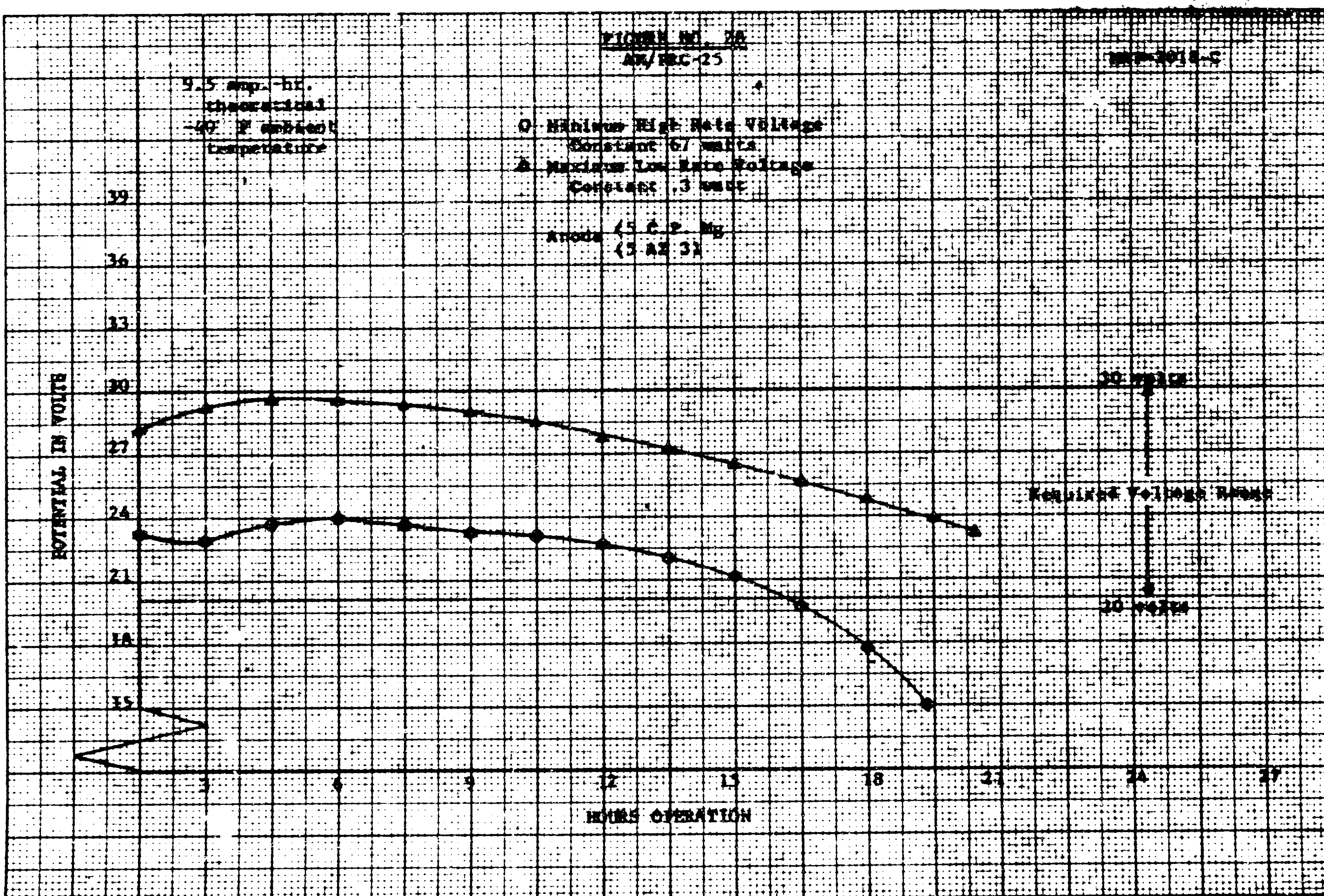


FIGURE NO. 28
AN/PRC-25
9.5 amp.-hr.
theoretical
-40° F ambient
temperature
O Minimum High Rate Voltage
Constant 67 watts
Δ Maximum Low Rate Voltage
Constant .3 watt
Anode {5 C.P. Mg
{5 AZ 3}
30 volts
Required Voltage Range
20 volts
POTENTIAL IN VOLTS
39
36
33
30
27
24
21
18
15
3
6
9
12
15
18
21
24
27
HOURS OPERATION

cells revealed that 97% of the magnesium was corroded (Figure No. 29). The inspection indicated that thicker magnesium and more Li_2CrO_4 would lengthen the discharge efficiency of the unit. Another unit, MAP-2018-E, was constructed utilizing .020" C.P. magnesium instead of .015" and a saturated solution of Li_2CrO_4. This insulated unit had to have the insulation removed after three hours of operation due to high temperature (Figure No. 30). While the MAP-2018-E design was most promising, further work is contemplated to finalize the AN/PRC-25 battery design.

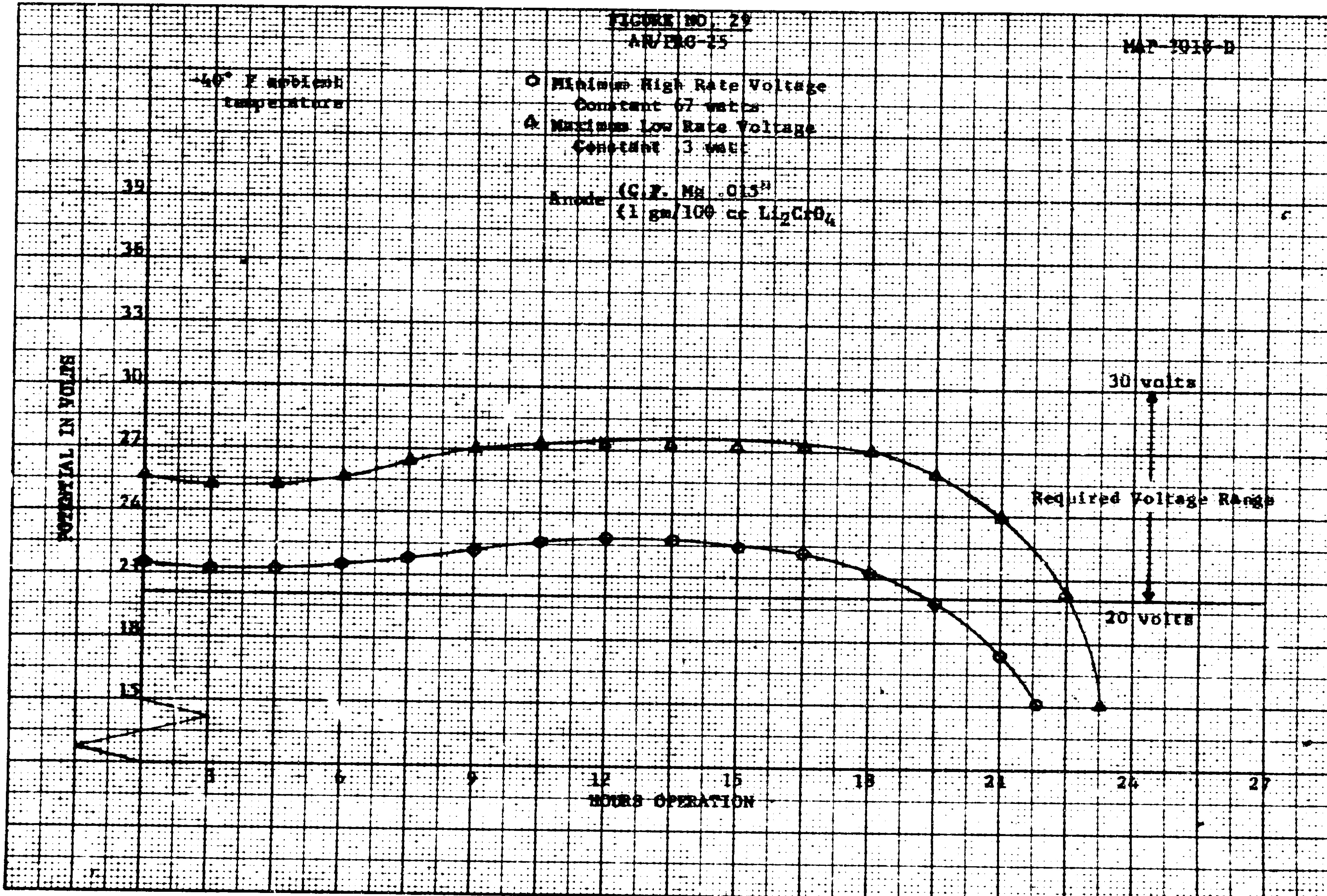


FIGURE NO. 29
AN/PRC-25
MAP-3018-D
-40° F ambient temperature
Minimum High Rate Voltage Constant 67 watts
Maximum Low Rate Voltage Constant 3 watt
Anode (C.P. Mg .015"
(1 gm/100 cc Li_2CrO_4
30 volts
Required Voltage Range
20 volts
POTENTIAL IN VOLTS
39
36
33
30
27
24
21
18
15
3
6
9
12
15
18
21
24
27
HOURS OPERATION

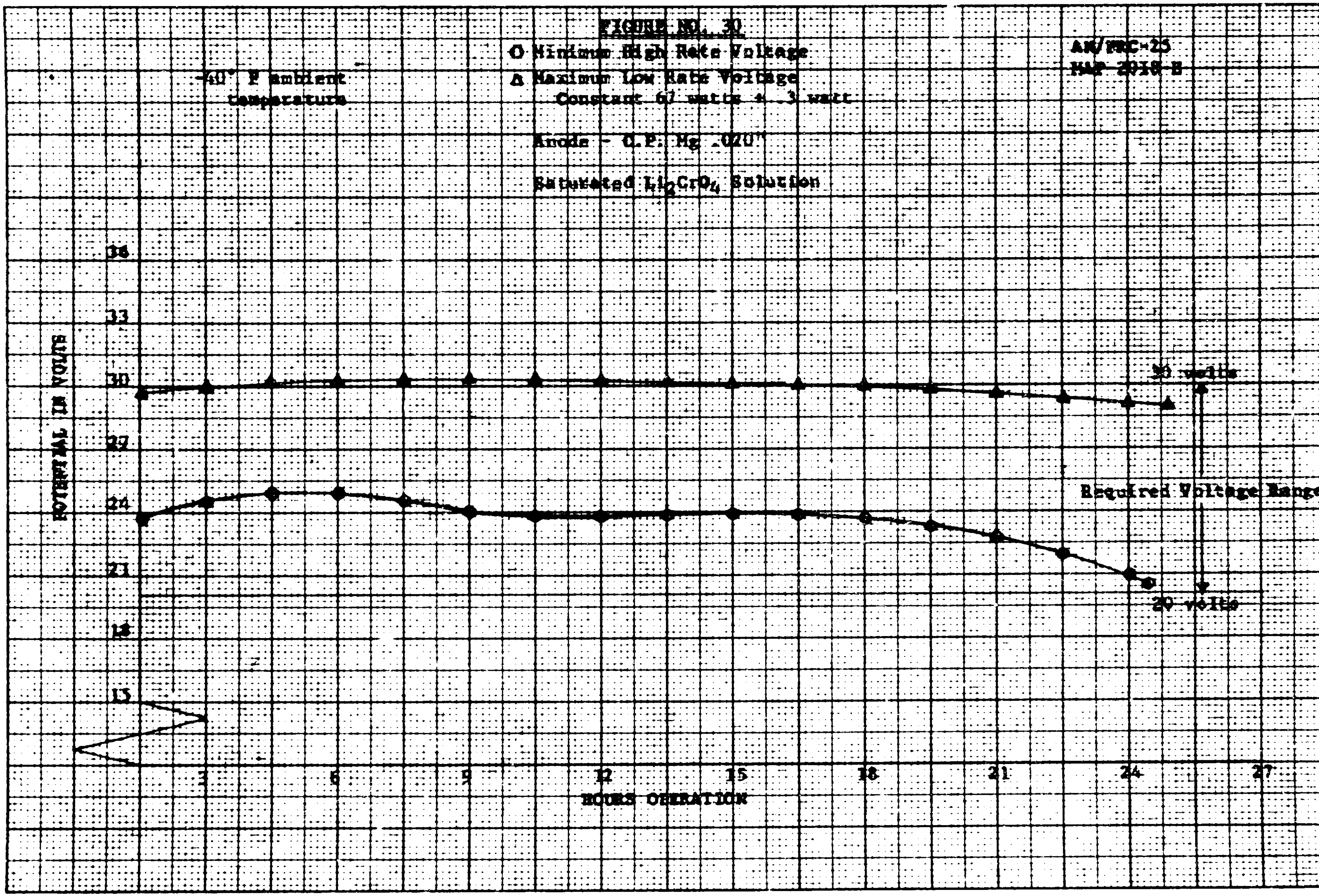


FIGURE NO. 30
O Minimum High Rate Voltage
Δ Maximum Low Rate Voltage
Constant 67 watts ± .3 watt
Anode - C.P. Mg .020"
Saturated Li_2CrO_4 Solution
-40° F ambient temperature
AN/PRC-25
MAP 2018-B
30 volts
Required Voltage Range
20 volts
POTENTIAL IN VOLTS
36
33
30
27
24
21
18
15
3
6
9
12
15
18
21
24
27
HOURS OPERATION

B. Development of MAP-2014 (62)

Efforts to date on MAP-2014 (62) have been centered around a final design assembly. A 9.5 ampere-hour battery weighing 3.2 pounds has been designed and developed to meet the AN/PRC-62 specification at a temperature range of -40° F to +125° F.

Cathodes and anodes are prepared and utilized as described in the Second Quarterly Progress Report.

Anode:	AZ 31 Height ...... 2.250" Width .... 1.562" Length ...... 0.015"

The magnesium plate has a .015" silver wire lug spot-welded on. The silver wire and magnesium are coated with EC 1004 at the spot-weld to prevent local action.

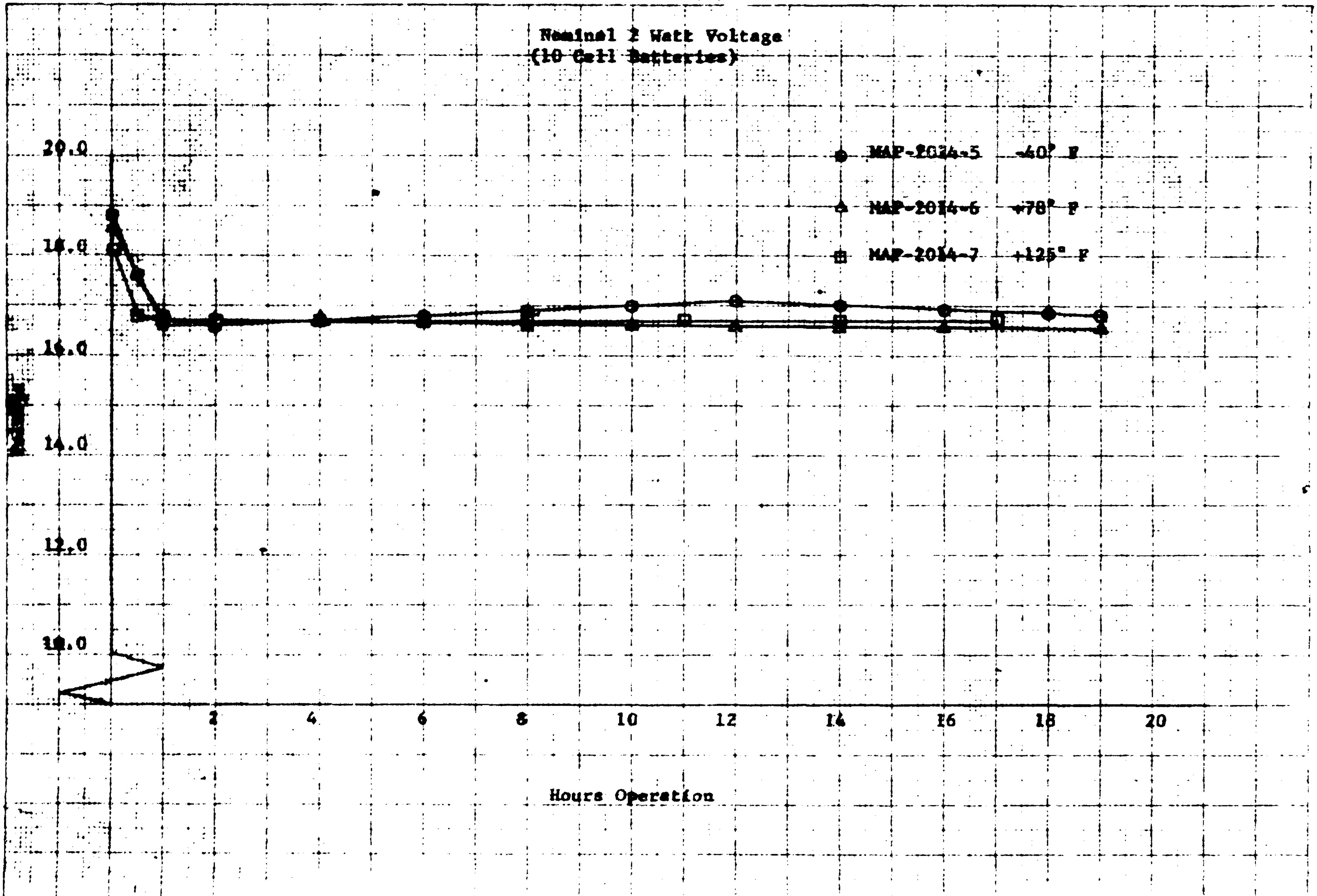
Cathode:	Yellow Mercuric Oxide (HgO) Height ...... 2.250" Width .... 1.562" Length ...... 0.025"
Separation:	Filter Paper 0.004"
Electrolyte:	Four normal magnesium perchlorate has been chosen as the desired electrolyte concentration.

Ten cells utilizing nine positives and ten negative plates per cell have been chosen as the final battery design to meet the MAP-2014 (62) application.

The battery has been discharged at three typical temperature specifications, -40° F, +75° F and +125° F. Optimum efficiency at these temperatures was obtained, as shown in Figure Nos. 31 and 32.

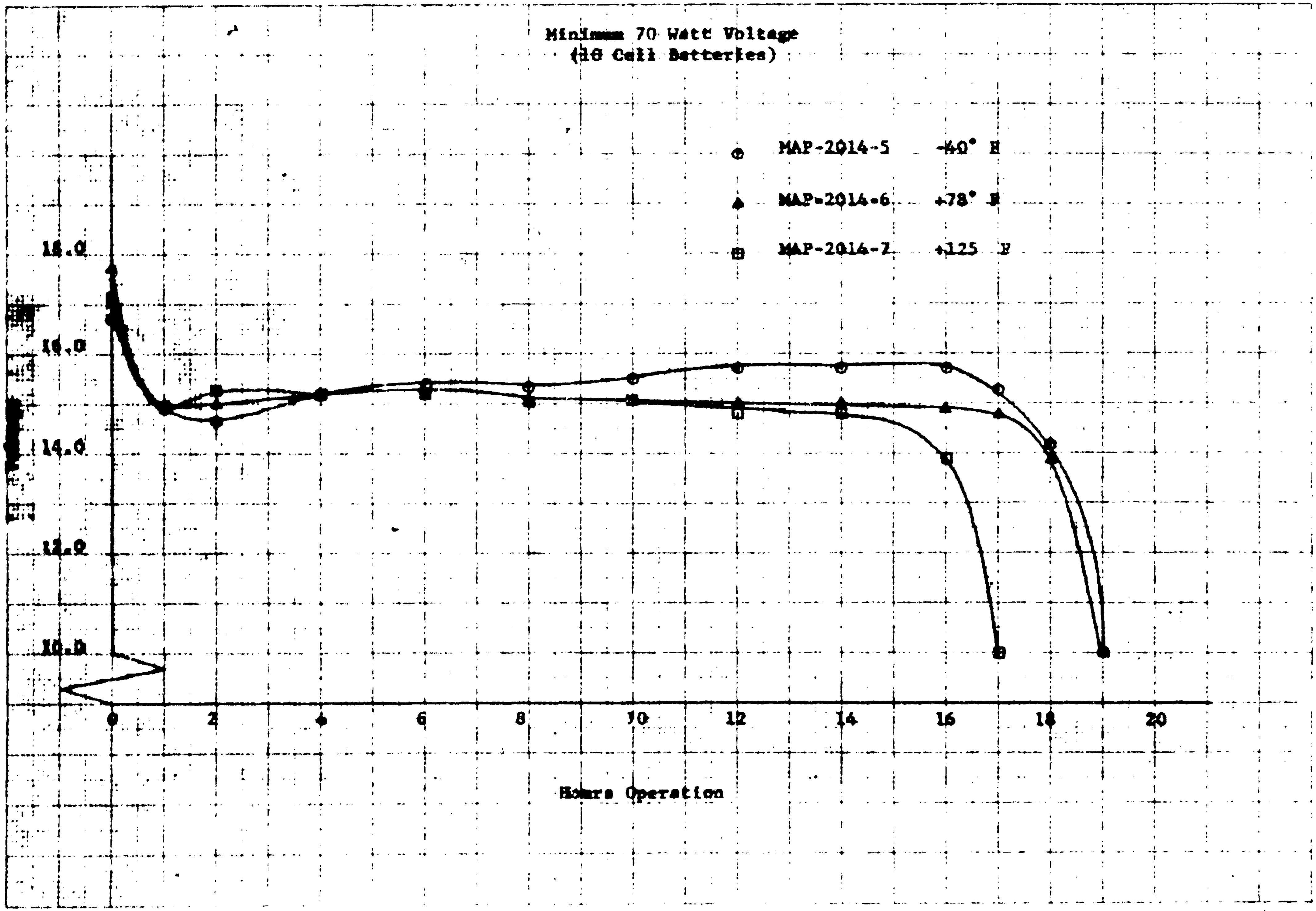
An attempt was made to simplify the cell design and construction. Instead of utilizing an electrolyte reservoir as in the photograph, Figure No. 33,

FIGURE NO. 31



Nominal 2 Watt Voltage
(10 Cell Batteries)
MAP-2014-5 -40° F
MAP-2014-6 +78° F
MAP-2014-7 +125° F
20.0
18.0
16.0
14.0
12.0
10.0
2
4
6
8
10
12
14
16
18
20
Hours Operation

FIGURE NO. 32



Minimum 70 Watt Voltage
(18 Cell Batteries)
MAP-2014-5 -40° F
MAP-2014-6 +78° F
MAP-2014-7 +125 F
18.0
16.0
14.0
12.0
10.0
0
2
4
6
8
10
12
14
16
18
20
Hours Operation

FIGURE NO. 33
SINGLE CELLS UTILIZING AN
ELECTROLYTE RESERVOIR

The Eagle-Picher Co.
Joplin, Mo.

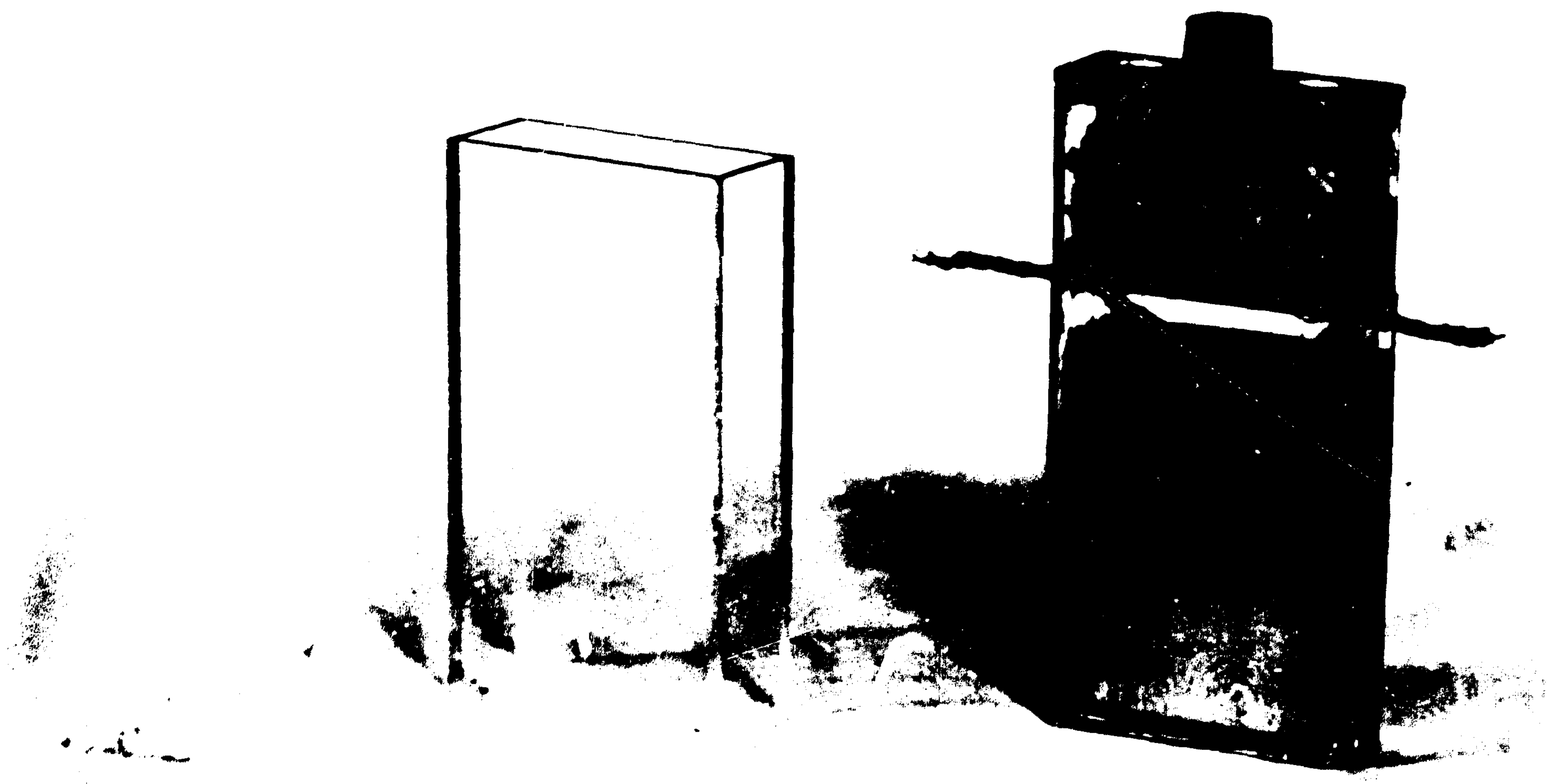


FIGURE NO. 34
COMPARISON OF ORIGINAL (RIGHT)
AND NEW (LEFT) CELL DESIGN

The Eagle-Picher Co.
Joplin, Mo.

the dry $Mg(ClO_4)_2$ was inserted directly into the cell on top of the plates. Figure No. 34 shows a comparison between the original and new cell design.

There was no noticeable difference in the efficiency of the two designs. Therefore, the new cell case was adopted.

Dimensions:

Height ...... 3.563"
Width .... 1.812"
Length ...... 0.656"

C. Development of MAP-2019 (5)

Several possible designs have been investigated to meet the PPS-5 application (pgs. 79 - 83). Design No. 1, pg. 79, utilizes 4/0 expanded silver-plated nickel grids discharged at 70% efficiency. It was decided to increase the number of plates from 18/19 (positive/negative) to 21/22, as described in Design No. 2, pg. 80. This unit discharged at 88% efficiency and there was more capacity than was needed. Therefore, it was decided to reduce the number of plate ratio to 19/20, as described in Design No. 3, pg. 81.

A unit was constructed utilizing 19/20 (positive/negative) plates. This unit discharged at 63% efficiency. These three previous discharges reveal an irregularity or inconsistency when we utilize the plated nickel grid.

There have been several possible explanations for this. One explanation is that the failure is due to the chemical reaction between the nickel grid and the complex ions of the electrolyte. Further investigations are being carried on.

The 4/0 silver wire was then utilized as described in Design Nos. 4 and 5, pgs. 82 and 83. These units were constructed but were not discharged during the period prior or during the preparation of this report.

ELEMENT DESIGN DATA SHEET

TYPE COUPLES: $HgO/Mg(ClO_4)_2$ Mg **DATE:** January 4, 1965

Design No. 1	.... PPS-5-1
No. Plates/Cell Pos/Neg	.... 18/19 382/403 in^2
Plate Size Height/Width-in.	.... 4.25" x 5.0" 21.25 in^2
Pos. Plate Thickness-in.	.... 0.032"
Neg. Plate Thickness-in.	.... 0.015"
Type Grid P/N	.... 4/0 Expanded Nickel, .005" Ag Flashed
Container - Type	.... Y-12
Inside Height-in.	.... 4.625" Res. 1.625"
Inside Width-in.	.... 5.23"
Inside Length-in.	.... 1.437"
Pos. Material-gm/sq.in. as	.... 1.75 (pulled down 1.80)
Neg. Material-gm/sq.in. as	.... 0.428 x 96% = 0.41 gm/in^2 as Mg
Pos. Material - gm/cell	.... 617 as HgO
Neg. Material - gm/cell	.... 165 as Mg
Theoretical Cap.-Pos/Neg A.H.	.... 153/362
Pos. Mat. Density-gm/cu.in.	.... 59 as blend
Neg. Mat. Density-gm/cu.in.	.... 28.6
cc of H_2O per cell	.... 230 + 103 gm $Mg(ClO_4)_2$ 50%
Total Cell Weight - lbs.	.... 3.34 activated
Expected Capacity-A.H.	.... 120 @ 10 amp with ± 5% voltage reg.
Estimated Watt-Hours/Lb.	.... 57.5 @ 12 hours
Formation	.... Vacuum Slurry
Type Insulation	.... 0.004" Filter Paper
Layers - Wet Thickness-in.	.... Filter Paper .004" x 2 x 18 .144 Cathodes .032" x 18 .576 Anodes .015" x 19 .285

Pos. Blend
HgO - 92%
Carbon - 6%
CMC - 1.5%
Fiber - 0.5%

Cell Length-in.	.... 1.005
Tolerance-in.	.... 0.432 or 30% of cell case length

ELEMENT DESIGN DATA SHEET

TYPE COUPLES: HgO Mg $(ClO_4)_2$ Mg **DATE**: January 7, 1965

Design No. 2	.... PPS-5-7
No. Plates/Cell Pos/Neg	.... 21/22 381/399
Plate Size Height/Width-in.	.... 3.625" x 5" 18.15 in^2
Pos. Plate Thickness-in.	.... 0.032
Neg. Plate Thickness-in.	.... 0.015
Type Grid P/N	.... 4/8 Expanded Nickel .005" Ag Flashed
Container - Type	.... Y-12
Inside Height-in.	.... 4.00 Res. 1.25"
Inside Width-in.	.... 5.23
Inside Length-in.	.... 1.437
Pos. Material-gm/sq.in. as	.... 1.75 (pulled down 1.80)
Neg. Material-gm/sq.in. as	.... 0.428 x 96% = 0.41 gm/in^2 as Mg
Pos. Material-gm/cell	.... 613 as HgO
Neg. Material-gm/cell	.... 163 as Mg
Theoretical Cap.-Pos/Neg A.H.	.... 152/359
Pos. Mat. Density-gm/cu.in.	.... 59 as blend
Neg. Mat. Density-gm/cu.in.	.... 28.6
cc of H_2O per cell	.... 230 + 103 gm Mg $(ClO_4)_2$ 50% compressed
Total Cell Weight-lbs.	.... 3.28
Expected Capacity-A.H.	.... 120 @ 10 amps with ± 5% voltage regulation
Estimated watt-hours/lb.	.... 57.5 @ 12 hours
Formation	.... Vacuum Slurry
Type Insulation	.... 1 layer 0.004" filter paper
Layers-Wet Thickness-in.	.... Filter Paper .004" x 2 x 21 0.168 Cathodes .032" x 21 0.672 Anodes .015" x 22 0.330
Cell Length-in.	.... 1.170
Tolerance-in.	.... 0.267 or 18.5% cell case length

ELEMENT DESIGN DATA SHEET

TYPE COUPLES: $Mg/Mg(ClO_4)_2/HgO$ DATE: January 18, 1965

Design No. 3	.... PPS-5-4
No. Plates/Cell Pos/Neg	.... 19/20
Plate Size Height/Width-in.	.... 5.0 x 3.625 345/363
Pos. Plate Thickness-in.	.... 0.032
Neg. Plate Thickness-in.	.... 0.015
Type Grid P/N	.... 4/0 Expanded Nickel Ag Flashed .005"
Container - Type	.... Y-12
Inside Height-in.	.... 4.0 Res. 1.25"
Inside Width-in.	.... 5.22
Inside Length-in.	.... 1.437
Pos. Material-gm/sq.in. as	.... 1.65 92% HgO
Neg. Material-gm/sq.in. as	.... 0.43 x 96% = 0.413 as Mg
Pos. Material-gm/cell	 524
Neg. Material-gm/cell	 150
Theoretical Cap.-Pos/Neg A.H.	.... 130 A.H./330 A.H.
Pos. Mat. Density-gm/cu.in.	 59
Neg. Mat. Density-gm/cu.in.	.... 28.6
cc of H_2O per cell	.... 230 + 103 gm $Mg(ClO_4)_2$
Total Cell Weight-lbs.	.... 3.50 lbs. Activated
Expected Capacity-A.H.	.... 120 A.H. @ 10 A. to 10% voltage
Estimated Watt-Hours/Lb.	.... 57.5 @ 12 hours
Formation	.... Vacuum Slurry ballmilled 16 hours
Type Insulation	.... Filter Paper
Layers-Wet Thickness-in.	.... One .004

Filter Paper	.004 x 2 x 19	.152"
Cathodes	.032 x 19	.608"
Anodes	.015 x 20	.300"

HgO = 92%
C = 6%
CMC = 1.5%
F = 0.5%

Cell Length-in.	.... 1.060
Tolerance-in.	.... 0.377 or 26.2% Void

ELEMENT DESIGN DATA SHEET

TYPE COUPLES: $Mg/Mg(ClO_4)_2/HgO$ **DATE**: January 21, 1965

Design No. 4	.... PPS-5-5
No. Plates/Cell Pos/Neg	.... 18/19
Plate Size Height/Width-in.	.... 4.25 x 5.0 21.25 in^2
Pos. Plate Thickness-in.	.... 0.032
Neg. Plate Thickness-in.	.... 0.015
Type Grid P/N	.... 4/0 Expanded Silver .005" .42 gm/in^2
Container-Type	.... Y-12
Inside Height-in.	.... 4.625 1.250" res.
Inside Width-in.	.... 5.23
Inside Length-in.	.... 1.437
Pos. Material-gm/sq.in. as	.... 1.75 88% HgO .218 AH/gm Blend Wt.
Neg. Material-gm/sq.in. as	.... 0.43 x 96% = 41 gm/in^2 as Mg
Pos. Material-gm/cell	.... 670 gm-as HgO 590 gm
Neg. Material-gm/cell	.... 166 as Mg
Theoretical Cap.-Pos/Neg A.H.	.... 146/365
Pos. Mat. Density-gm/cu.in.	 59
Neg. Mat. Density-gm/cu.in.	.... 28.6
cc of H_2O per cell	.... 260 + 116 gm Mg(ClO) 50% compressed, 2.6 gm Li_2CrO_4
Total Cell Weight-lbs.	.... 3.54 lbs. activated
Expected Capacity-A.H.	.... 120 A.H. @ 10 A. to 10% voltage drop
Estimated Watt-Hours/Lb.	.... 57.5 @ 12 hours
Formation	.... Vacuum Slurry
Type Insulation	.... .004" Filter Paper
Layers-Wet Thickness-in.	.... Filter Paper .004 x 2 x 18 .144 Cathodes .032 x 18 .576 Anodes .015 x 19 .285 88% HgO 10% C 1.5% CMC 0.5% Fiber
Cell Length-in.	.... 1.005
Tolerance-in.	.... 0.432 or 30% of cell length

ELEMENT DESIGN DATA SHEET

TYPE COUPLES: $Mg/Mg(ClO_4)_2/HgO$ **DATE**: January 27, 1965

Design No. 5	.... PPS-5-6
No. Plates/cell Pos/Neg	.... 19/20
Plate Size Height/Width-in.	.... 4.00 x 5.00 20 in^2
Pos. Plate Thickness-in.	.... 0.030
Neg. Plate Thickness-in.	.... 0.015
Type Grid P/N	.... 4/0 Expanded Ag .005" .42 gm/in^2
Container - Type	.... Y-12
Inside Height-in.	.... 4.375
Inside Width-in.	.... 5.23
Inside Length-in.	.... 1.437
Pos. Material-gm/sq.in. as	.... 1.70 (pulled down 1.80)
Neg. Material-gm/sq.in. as	.... .43 x 96% = .41 gm/in^2 as Mg
Pos. Material-gm/cell	.... 646 gm - 594 gm HgO
Neg. Material-gm/cell	.... 164 as Mg
Theoretical Cap.-Pos/Neg A.H.	.... 147/461
Pos. Mat. Density-gm/cu.in.	 61
Neg. Mat. Density-gm/cu.in.	.... 28.6
cc of H_2O per cell	.... 260 x 116 gm $Mg(ClO_4)_2$ 50% compressed + 2.6 Li_2CrO_4
Total Cell Weight-lbs.	.... 3.48 lbs. activated
Expected Capacity-A.H.	..........120 A.H. @ 10 A. to 10% voltage
Estimated Watt-Hours/Lb.	.... 57.5 @ 12 hrs.
Formation	.... Vacuum Slurry
Type Insulation - 1 layer	.... .004" Filter Paper
Layers-Wet Thickness-in.	.... Filter Paper .004 x 2 x 9 .152 Cathodes .030 x 19 .570 Anodes .015 x 20 .300
	92% HgO 6% C 1.5% CMC 0.5% Fiber
Cell Length-in.	.... 1.022
Tolerance-in.	.... .415 or 29% of cell case length

D. Activated Stand Test

Two MAP-2014 (62) cells with a theoretical cathode capacity of 9.5 ampere-hours were constructed having AZ 31 and C.P. magnesium as anodes. The cells were activated with 4N magnesium-perchlorate electrolyte containing 1% lithium chromate and were discharged at 1.5 amperes after various stand times.

An activated stand time of one week revealed a discharge efficiency of 92% for the AZ 31. The cell utilizing C.P. magnesium revealed complete corrosion of the magnesium.

E. Additive Study

An analysis of the heat evolved during discharge shows that the heat is due to the irreversibility of the magnesium anode and the corrosion reaction. The heat problem must be controlled for high efficiency, particularly at high discharge rates.

In an attempt to control the heat Li_2CrO_4 was added to the $Mg(ClO_4)_2$. An experiment was set up to obtain the relationship between percents of Li_2CrO_4 and magnesium corrosion as gas evolved.

Oxidation Rate of Pure Magnesium

$\frac{\text{Gms. } Li_2CrO_4}{\text{Liter } Mg(ClO_4)_2 \text{ 4N}}$	
0	2.37 cc/min
0.020	1.95 cc/min
0.100	0.791 cc/min
0.200	0.0646 cc/min
1.00	0.013 cc/min

VI. SUMMARY

The magnesium/magnesium perchlorate/mercuric oxide battery system exhibited good capacity and voltage tolerance for most of the discharge rates at +75° F.

Low temperature and high temperature studies of these batteries, conducted at the same discharge rates, demonstrated that this system operates at high efficiency over a temperature range of -40° F to +125° F.

An activated stand of one week with less than 10% capacity loss can be expected from a mercuric oxide cell utilizing AZ 31.

VII. CONCLUSIONS

Work over the past three quarters has indicated the following:

1. The magnesium/magnesium perchlorate system will operate at high efficiencies over the temperature range of -40° F to +125° F.

2. The output of the battery is between 30 and 75 watt-hours/pound at medium rates of discharge.

3. Failure modes of the battery have indicated that so far the reliability of the system is high and no critical failure modes have been found to date.

VIII. PROGRAM FOR NEXT INTERVAL

Modular battery construction for the following:

AN/PRC-62 Application	MAP-2014
AN/PRC-25 Application	MAP-2018
PPS-5 Application	MAP-2019

IX. PERSONNEL

NAME	TITLE	MAN-HOURS
Cupp, E. B.	Project Engineer	273
Sharpe, J. R.	Design Engineer	512
Dines, J. M.	Engineering Manager	37
Morse, E. M.	Senior Engineer	21
McCleary, E.	Battery Engineer	215
Gosch, C. O.	Staff Engineer	10
Hodges, K.	Technician	522
	TOTAL	1,590